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# Gas Chromatograph-Based System for Measuring the Methane Fraction of Diesel Engine Hydrocarbon Emissions

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# A Gas Chromatograph-Based System for Measuring the Methane Fraction of Diesel Engine Hydrocarbon Emissions

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16. ABSTRACT

An instrument has been developed (termed the "methane analytical system") enabling diesel methane emissions to be quantified separately from total unburned hydrocarbon emissions. The instrument employed gas chromatographic principles whereby a molecular sieve column operating isothermally separated methane from the nonmethane hydrocarbons. Direct on-line sampling occurred via constant volume sample loops. The effluent was monitored with a flame ionization detector.

The instrument was fully calibrated (i.e., extremely linear response over a large concentration range) for use with Diesel engines as part of an on-going alternative fuels research program. Methane emissions from a light-duty, multicylinder, indirect-injected Diesel engine fumigated with natural gas were measured on-line using the methane analytical system. Methane emissions were found to range from as low as 250 ppm to a high of nearly 2%. The nonmethane hydrocarbon emissions were determined by subtracting the methane level from the total unburned hydrocarbon level. In the event that the federal engine certification procedures are changed to be based on nonmethane hydrocarbon emissions, a methane analytical system such as the one described here would have great utility.


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Abstract

Investigations have concluded that methane does not appear to be photochemically reactive in the atmospheric system and does not participate in smog formation. Since methane is "nonreactive," and may in the future be excluded from the total unburned hydrocarbon emissions, an instrument was designed and developed (termed the "methane analytical system") enabling methane emissions to be quantified separately from total unburned hydrocarbon emissions. The instrument employed gas chromatographic principles whereby a molecular sieve column operating isothermally separated methane from the nonmethane hydrocarbons. Direct on-line sampling occurred via constant volume sample loops. The effluent was monitored with a flame ionization detector.

The instrument was fully calibrated (i.e., extremely linear response over a large concentration range) for use with Diesel engines as part of an ongoing alternative fuels research program. Methane emissions from a light-duty, multicylinder, indirect-injected Diesel engine fumigated with natural gas were measured on line using the methane analytical system. Methane emmisions were found to range from as low as 250 ppm to a high of nearly 2%. The nonmethane hydrocarbon emissions were determined by subtracting the methane level from the total unburned hydrocarbon level. In the event that the federal engine certification procedures are changed to be based on nonmethane hydrocarbon emissions, a methane analytical system such as the one described here would have great utility.

## Introduction

It is well known that hydrocarbon emissions result from internal combustion engines. Within the engine, sources of these emissions include incomplete combustion, wall quench, lean misfire, and pyrolysis of the lubricating oil. They exist in the gas pase in both spark-ignited and Diesel engine exhaust and also as adsorbates on particles.

The main concern with unburned hydrocarbons in the atmosphere is that they photochemically decompose leading to smog formation (1).* As a result Air Quality Standards have been established for these pollutants in attempting to reduce them through the control of hydrocarbon emissions (2). However, numerous studies have shown that each individual hydrocarbon compound has different degrees of relative photochemical reactivity (3-7). There are several methods for assigning relative reactivities to each hydrocarbon compound, with the concensus indicating that methane, ethane, propane, acetylene, and benzene are "photochemically nonreactive" hydrocarbons (1,3-8). These results prompted California to implement a nonmethane hydrocarbon standard in 1980 (8). In addition, consideration is being given to federal certification procedures for motor vehicles based on nonmethane hydrocarbon emissions (9). In view of these considerations, an instrument allowing gaseous unburned methane emissions to be measured separately from total unburned hydrocarbons would be of great utility. A subtractive technique would then yield total nonmethane hydrocarbon emissions present in motor vehicle exhaust. The research presented here provides an instrument, termed the "methane analytical system," which would allow determination of the unburned hydrocarbon methane separately from the total unburned hydrocarbons present in gaseous exhaust.

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*Numbers in parentheses refer to entries in the reference list at the end of the paper.

INSTRUMENT DEVELOPMENT

The core of the system consists of the gas chromatographic molecular sieve column responsible for separation of methane from the nonmethane unburned hydrocarbons. The column used was a stainless steel column 6.0 ft long by 0.125 in. o.d. packed with Supelco Molecular Sieve 5A on Supelcoport 80/100 mesh (supplied by Supelco, State College, PA). A molecular sieve column was chosen, because it exploits the size differential between methane and all heavier unburned hydrocarbons.

The molecular sieve column separates the air (oxygen and nitrogen) and carbon monoxide from the methane and passes these constituents to the FID and all heavier unburned hydrocarbons are trapped in the column. By reversing the direction of the carrier gas through the column (backflushing), the heavier unburned hydrocarbons are purged from the column and vented to waste. The gases in order of elution from the column into the FID analyzer are oxygen, which may give a small peak; methane; and carbon monoxide (10).

The column is housed within an insulated oven in order to maintain isothermal operation. A pictorial representation of the entire separation system is included in Figure 1. The oven housing is fabricated from a metal cylindrical drum approximately 30 cm in both height and diameter. Covering all interior surfaces of the drum is rigid foam insulation approximately 1.9 cm thick. Its primary purpose is to minimize heating losses while maintaining isothermal conditions above the surrounding ambient temperature.

The heating source is a simple incandescent light bulb in a porcelain socket mounted in the bottom of the oven. A 60 Watt frosted light bulb was found to be more than adequate in maintaining the chosen oven

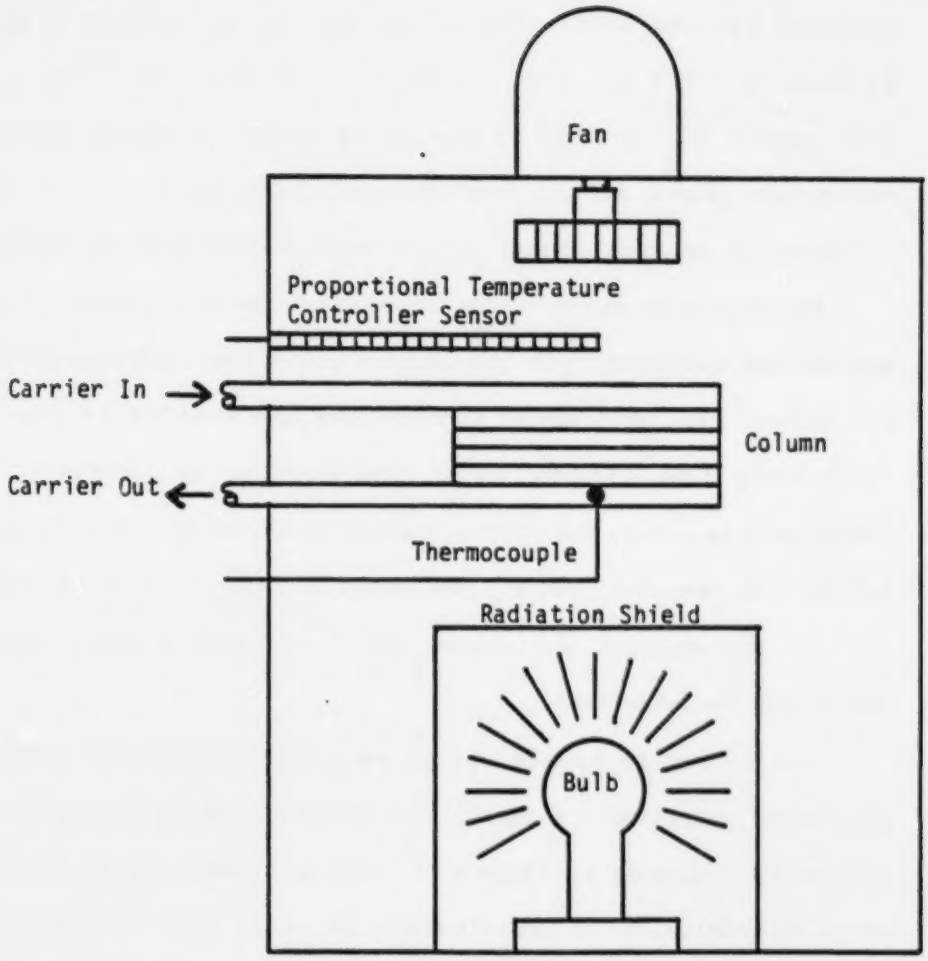


Fig. 1 Separation Section of Methane Analytical System.

temperature of 46°C. To minimize radiative heating effects, a metal shield was constructed and positioned to surround the light bulb.

In order to attain temperature uniformity within the entire oven, a 62 W, Oster Model No. 2 recirculating fan was mounted on the lid of the metal drum. An Athena Model No. 57-3 proportional temperature controller with accompanying probe were utilized in order to maintain steady state oven temperature. Its sensing element was mounted in the side of the oven directly above the column. The temperature controller adjusts the current to the light bulb with the current being inversely proportional to temperature. In addition to the sensing element, a thermocouple was attached directly onto the column and its temperature was monitored by an Omega 871 Digital Thermometer.

Prior to the oven section are various plumbing accessories used to introduce the sample into the carrier (nitrogen) stream. Central to this sample introduction are two six-port gas sampling valves (A and B). Illustrated in Figure 2 are the various flowstreams of the methane analytical system. The sample line and the carrier stream consist of Teflon (a material nonreactive with hydrocarbons) and stainless steel tubing respectively, while the detector fuel and detector air lines are plastic. Valves A and B are shown to be in their sample-loading and carrier-foreflush positions respectively. Each valve can be switched from one position employing three of the ports to another position employing the other three ports. Valve A also has a sample loop included for sample loading and subsequent injection into the carrier stream. Valve B is included to enable the reversal of the carrier flow direction through the column. This flow reversal, or "backflushing," of the column purges any

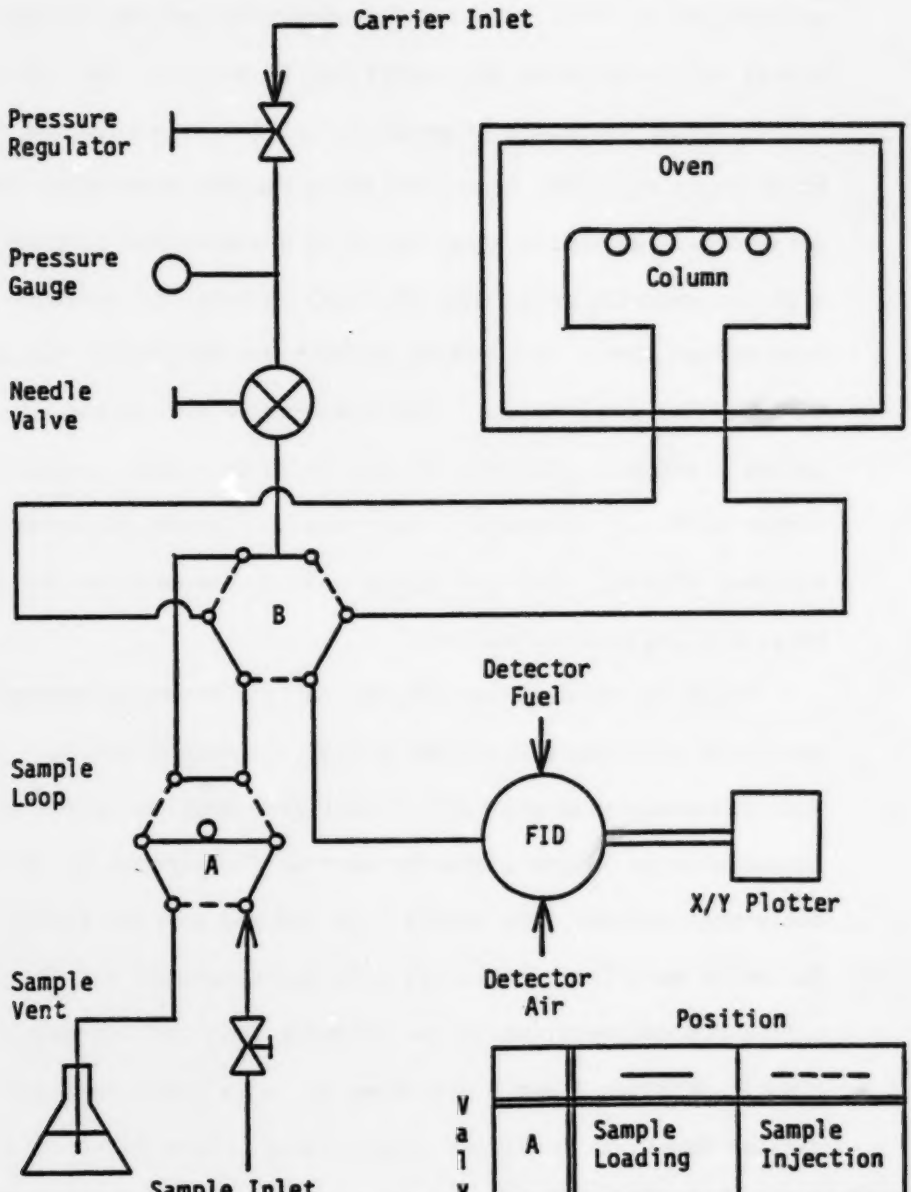


Fig. 2 Methane Analytical System.

retained substances (i.e., nonmethane hydrocarbons) from the column. The operation of the valves (A and B) are discussed in detail in Ref.(11).

Figure 3 is a schematic detailing the various valve positions as they appear on the front panel of the methane analytical system. All gas streams eminate from the gas phase instrumentation cart, details of which are given in Ref. (11).

A cold trap precedes both the total hydrocarbon analyzer and methane analytical system. This trap condenses any vaporized water originally present in the exhaust. Therefore, exhaust concentrations (both methane and total unburned hydrocarbons) are reported on a water-free or dry molar basis. However, the span gases do not pass through the cold trap but are still utilized on a dry molar bases.

A Beckman Model 109 FID hydrocarbon analyzer was used for detection of sample constituents eluting from the molecular sieve column. The detection signal from the FID was fed into an Autograf Model 2D X-Y recorder. The X-axis was set on a calibrated time base (sec/div) while the Y-axis was assigned detector response (MVDC/div).

## INSTRUMENT CALIBRATION

Prior to data acquisition, the methane analytical system was fully calibrated for both repeatability and correct quantification of data. The instrument was then used to quantify exhaust gas samples from a light-duty, multicylinder, IDI Diesel engine fumigated with natural gas (12).

The first step was to calibrate the instrument using various sample loops with known internal volumes. These sample loops reduced the number of required span gases (gas bottles consisting of various methane

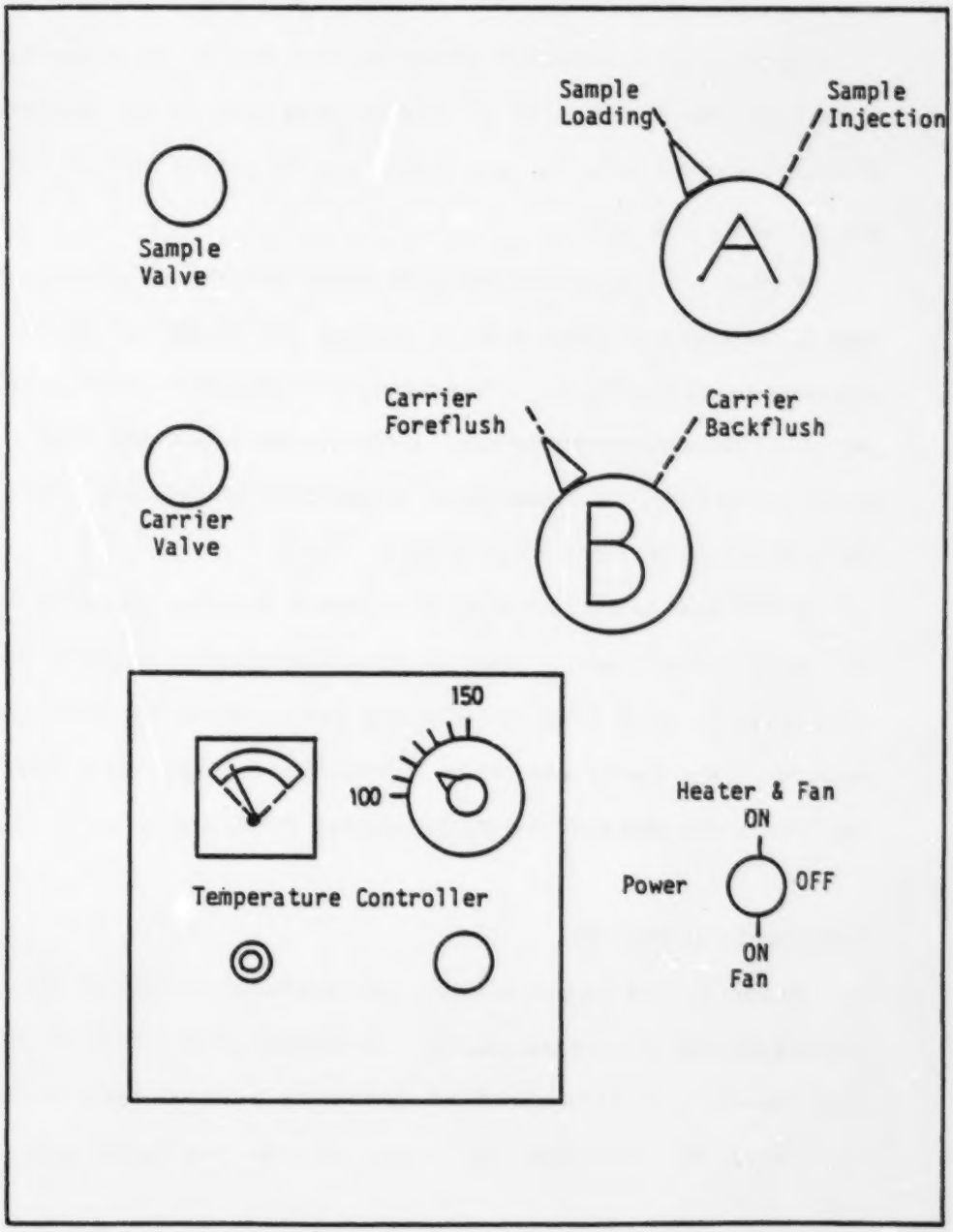


Fig. 3 Front Instrumentation Panel of Methane Analytical System.

concentrations in nitrogen). Normally the internal volume of sample loops are not determined to such great precision, a result of usually having numerous high pressure calibrated span gases for use in a single sample loop. However, to reduce the required number of calibrated span gases (expensive), a set of differently sized sample loops was proposed.

The sample loops were made from commercial grade 0.125 in. (3.18 mm) o.d. by 0.035 in. (0.884 mm) wall thickness 316 stainless steel tubing. The tubing was conditioned by rinsing with pentane to remove any residual manufacturing oils. Seven straight sections of tubing were precisely cut for use in valve A. Lengths of 3, 4, 6, 9, 12, 24, and 36 in. (7.6, 10.2, 15.2, 22.8, 30.5, 60.9, and 91.4 cm) were chosen.

The internal volume of each sample loop was experimentally determined by filling the sample loop with distilled water at approximately 20°C and noting the difference from the empty dry weight. A Mettler type H15 balance with capability of mass determination of 0.1 mg was used for all weighing purposes. The difference in weight was a direct measurement of the internal loop volume (using the density of water to convert from units of mass to volume). Illustrated in Figure 4 is a plot of the sample loop volumes versus the various sample loop lengths. Clearly, the regression is linear with the curve passing through the origin.

Having established the proportionality existing between the various tube lengths and their respective internal volumes, the internal "dead" volume of valve A remained to be determined. Attempting to minimize this dead volume, stainless steel zero-volume nuts and ferrules were employed in the ports of the valve. However, an appreciable internal volume still

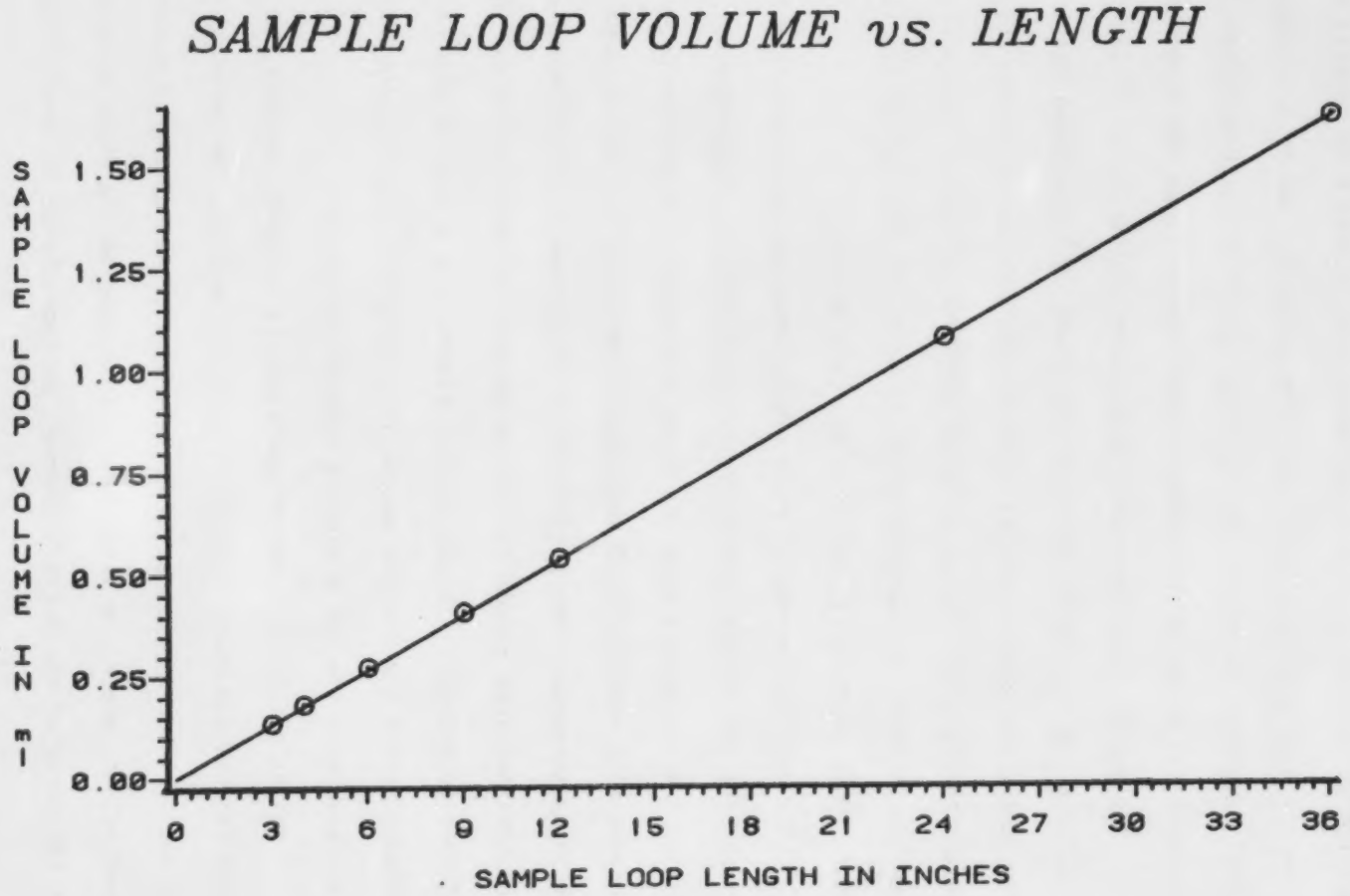


Fig. 4 Calibration of Sample Loops.

remained between the inlet and outlet valve ports. In a manner similar to that used for the sample loops internal volumes, the dead volume of the valve was experimentally determined to be equivalent to 0.1 ml. This amount was then added to each internal volume of the sample loops to account for the internal dead volume of valve A. A new proportionality could then be found between the various sample loop lengths and their respective total internal volumes. Once a single sample loop was chosen to be the standard loop and then calibrated with the span gases, the remaining loops could be used as though they were different span gas standards. The quantified amounts of these other standards (apparent concentrations) could easily be calculated by multiplying the standard sample loop concentration by the appropriate fraction of total internal volume of the different sized sample loop divided by the total internal volume of the standard sample loop. More simply, the ratio of the two loops' total internal volume was all that was necessary to define another concentration standard using

$$C_{app} = C_{std} \, (V_{app}/V_{std}) \qquad (1)$$

where

$C_{app}$ = Apparent Concentration,

$C_{std}$ = Standard Concentration,

$V_{app}$ = Apparent Total Internal Volume,

and

$V_{std}$ = Standard Total Internal Volume.

Two methane span gases were found to be sufficient to cover the range of exhaust emissions from Diesel engine operation. Span gases of 411 ppm and 8200 ppm methane in nitrogen (by volume) and the various sized sample loops were felt to provide an adequate number of calibration points.

The 24 in. sample loop was chosen as the standard sample loop to be used for the analysis of Diesel engine exhaust. The apparent concentrations of the other sample loops were calculated using Eq. 1. Given in Table 1 is a listing of all sample loops with their volumes corrected to account for the dead volume of valve A, along with the apparent methane concentrations for the two span gases. For example, the lower concentration of the smallest loop using Eq. 1 is

$$C_{app} = (411 \text{ ppm})\ (0.2386 \text{ ml})/(1.1711 \text{ ml}) = 84 \text{ ppm } CH_4/N_2 \text{ by volume.}$$

Numerous instrumental parameters had to be specified for daily operation of the methane analytical system. All gas streams were carefully controlled. Specifically, the carrier gas stream was calibrated to equal a volumetric flowrate of 80 ml/minute at the column exit using a soap bubble flow meter. Valves A and B were in their sample-loading and carrier-foreflush positions for this measurement. A high carrier flowrate was chosen in hope of reducing sample turn-around time without greatly sacrificing methane peak resolution. The detector fuel and detector air (zero grade) pressures entering the FID were kept constant at values of 18 and 12 psi respectively. These pressures were monitored constantly to insure no variation of the detector response characteristics. The pressure in the sample lines leading to both the methane analytical system and the total unburned hydrocarbon analyzer was kept constant at a value of 6 psi. Both the oven and nitrogen carrier were started approximately 12 hours prior to any data acquisition in order to allow adequate time for the column to thermally equilibrate.

Table 1

Apparent Methane Concentrations of Sample Loops

| Sample Loop Length* (in) | Sample Loop Internal Volume** (ml) | Apparent Concentration of 411 and 8200 ppm standards (ppm $CH_4$ in $N_2$ by Volume) | |
|---|---|---|---|
| 3 | 0.2386 | 84 | 1671 |
| 4 | 0.2828 | 99 | 1980 |
| 6 | 0.3720 | 131 | 2605 |
| 9 | 0.5051 | 177 | 3537 |
| 12 | 0.6381 | 224 | 4468 |
| 24*** | 1.1711 | 411 | 8200 |
| 36 | 1.7041 | 598 | 11932 |

*excludes dead-volume contribution of Valve A

**includes dead-volume contribution of Valve A

***standard sample loop

An X-Y Recorder was used as the output device. The range and sweep rate were held constant at 0.5 mVDC/div and 20 sec/div respectively. The FID attenuation was varied as necessary to keep the recorder from exceeding its full-scale value. However, once an attenuation scale was chosen on the FID, zero adjustment using the zero adjust knob always preceded every sample analysis. The procedure followed for sample analysis was as follows:

(1) With valves A and B placed in their sample-loading and carrier-foreflush positions respectively, the sample was introduced into valve A and purged the sample loop through the water breaker for approximately one minute.

(2) The sample valve was slowly closed until bubbles were barely escaping the tube exit.

(3) The appropriate FID attenuation scale was selected and zero adjusted.

(4) The following three changes were simultaneously made.

  (a) Valve A was switched from the sample-loading to the sample-injection position with no changes occurring in valve B.

  (b) The recorder pen was switched to a sweeping position.

  (c) A digital stopwatch was started.

(5) After complete detection of the methane peak (approximately 2.5 minutes), valve B was switched from the carrier-foreflush position to the carrier-backflush position with no changes occurring in valve A. This backflushing purged all heavier unburned hydrocarbons from the column.

(6) At time equal five minutes (2.5 minutes of column backflushing), valves A and B were simultaneously returned to their sample-loading and carrier-foreflush positions respectively. The recorder pen was returned to its starting position and zero-adjusted if necessary. The stopwatch was reset to zero time and the system was ready for the next sample injection.

A sample chromatogram is included in Figure 5 illustrating the detectors response during the analysis. A typical chromatogram would include a flat (noise-free) baseline until elution of a methane peak followed by a return to the baseline.

The loop method of sample introduction was chosen instead of syringes in the hope that injection repeatability would be better. Indeed, this proved to be so and it was found that peak height (measured in mm) as opposed to peak area could be used for quick and simple quantification without loss of accuracy. Peak height was defined as that distance from the peak maximum to the peak baseline. The peak baseline was defined as the plateau immediately preceding the peak. To account for different FID attenuation factors, the peak height, measured in mm, was multiplied by the FID attenuation (e.g., 1, 3, 10, 30, 100, etc.) and the X-Y recorder attenuation of 0.5. For example, if a peak height was measured to be 500 mm with the FID attenuation on X100 and the stripchart recorder attenuation on 0.5, the reported height used in a calibration curve for quantification would be 2500 mm (500x100x0.5=2500).

Included in Table 2 is an example of the two calibration gases employed in several of the different sized sample loops. All samples with five total injections each resulted in a variance of less than 2% standard deviation of the mean, illustrating good injection repeatability. The

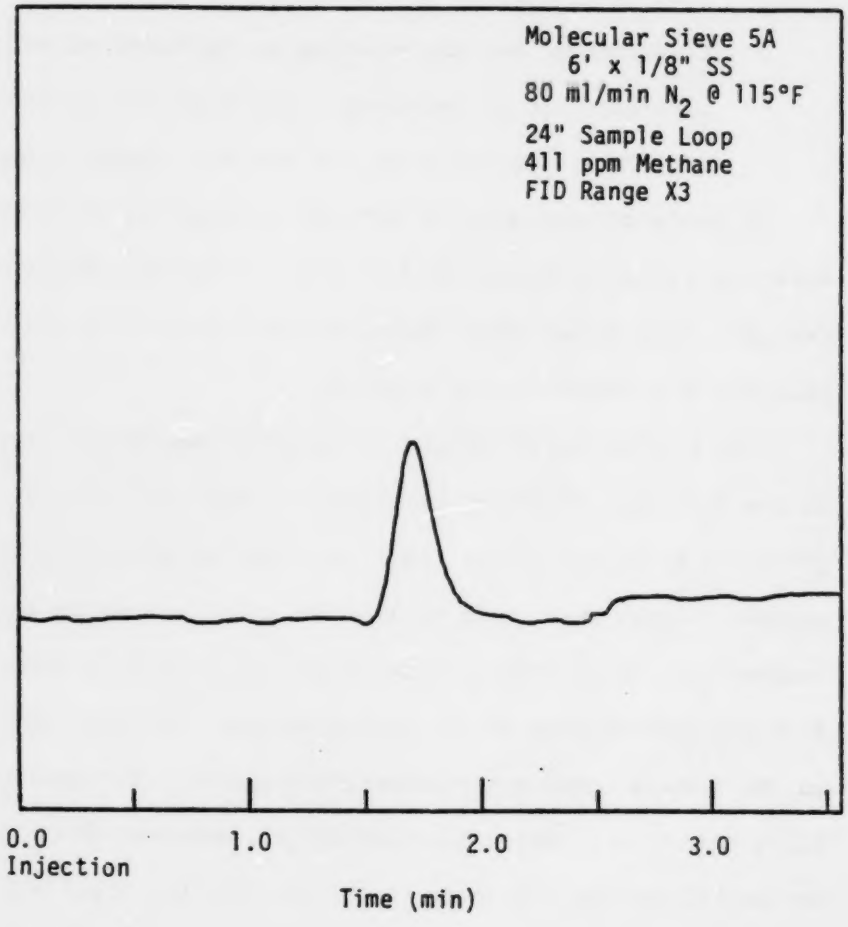


Fig. 5 Chromatogram of Methane Calibration Gas.

Table 2

Detector Response Calibration

| Sample Loop* Length (in) | Apparent Methane Concentration** (ppm $CH_4$ in $N_2$ by volume) | Sample Peak Height Mean*** (mm) | Standard Deviation of Mean (mm) | Percent Standard Deviation of Mean (%) |
|---|---|---|---|---|
| 4 | 99 | 127 | 1.79 | 1.41 |
| 6 | 131 | 165 | 2.31 | 1.40 |
| 9 | 177 | 230 | 2.51 | 1.09 |
| 9 | 3537 | 158 | 2.48 | 1.57 |
| 12 | 4468 | 195 | 2.33 | 1.19 |
| 24 | 411 | 180 | 3.25 | 1.80 |
| 24 | 8200 | 111 | 1.06 | 0.96 |

*excludes dead-volume contribution of Valve A

**obtained from Table 4.1

***Averaged from repetitive sampling population of 5, detector and recorder attenuation corrections not incorporated

data of Table 2 is plotted in Figure 6. Figure 7 is an enlargement of the smaller valued data plotted in Figure 6. The detector response curve is extremely linear over a wide attenuation range, again emphasizing the large linearity range of the FID.

## METHANE MEASUREMENTS OF DIESEL ENGINE EXHAUST GASES

As a part of an ongoing alternative fuels program, methane emissions from a light-duty, multicylinder, IDI Diesel engine fumigated with natural gas were measured using the methane analytical system (12). Included in Table 3 is a summary of the test engine specifications along with the steady-state operating conditions used in the engine study. Four brake power output levels (loads) at three different engine speeds defined the 12 conditions studied. Combustion, performance, and emissions data were collected at all 12 operating conditions. A point of maximum fumigant (natural gas) substitution was defined by increasing the ratio of fumigant over Diesel fuel until audible knock was detected. This was termed as the "maximum" condition. A second fumigant condition, "half-maximum," was established by utilizing only 50% of the "maximum" fumigant inlet flow to the engine.

Figure 8 includes sample chromatograms obtained during actual Diesel engine operation. Engine speed (RPM) and power output level (load) are printed on each illustration. Each of these chromatograms was for engine operation at the maximum natural gas substitution condition. The Diesel engine sample retention time duplicated the span-gas retention time, thereby providing a high degree of certainty that the eluted component was indeed methane.

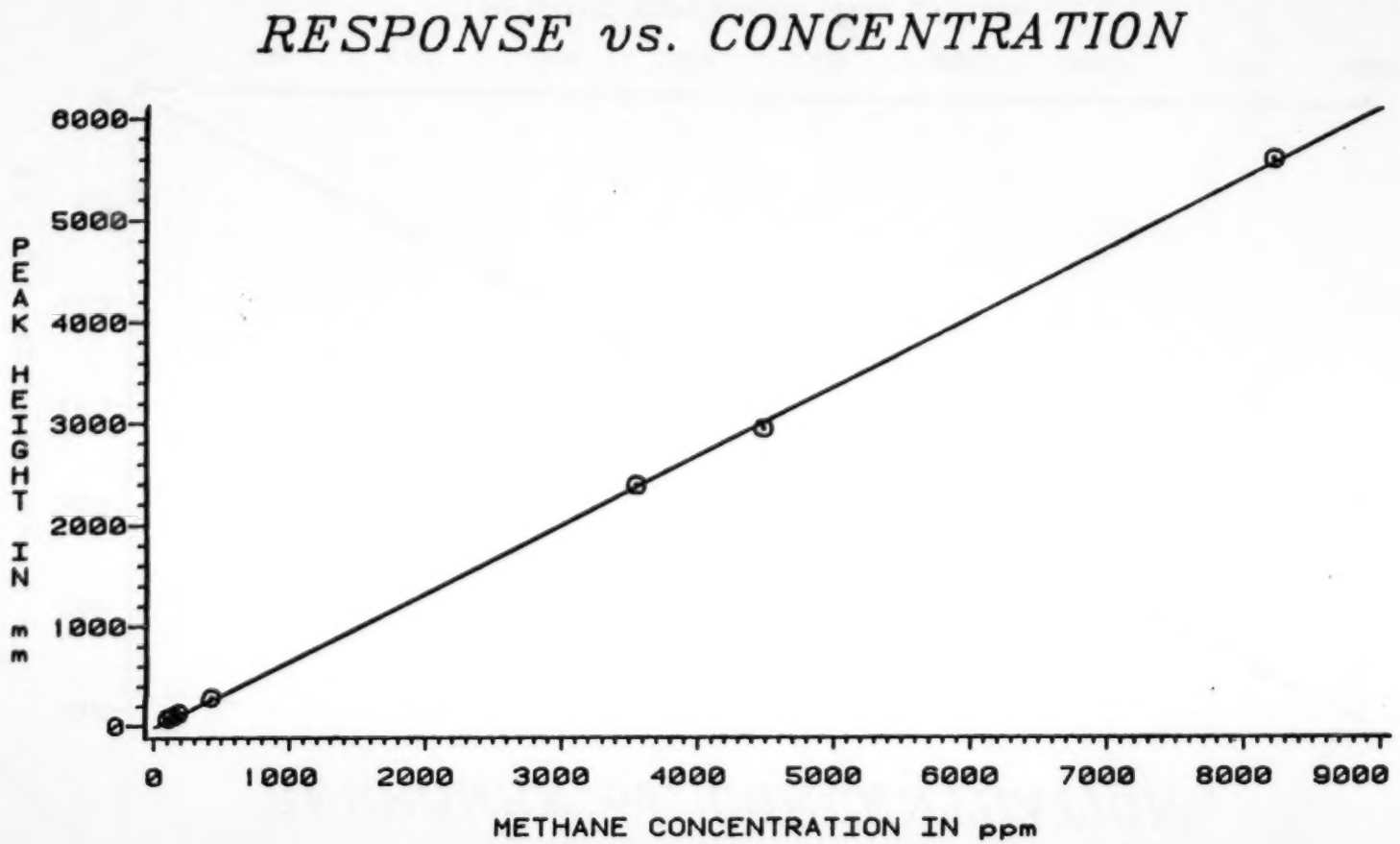


Fig. 6 Response of Methane Analytical System to Calibration Gases Ranging from 99 to 8200 ppm Methane.

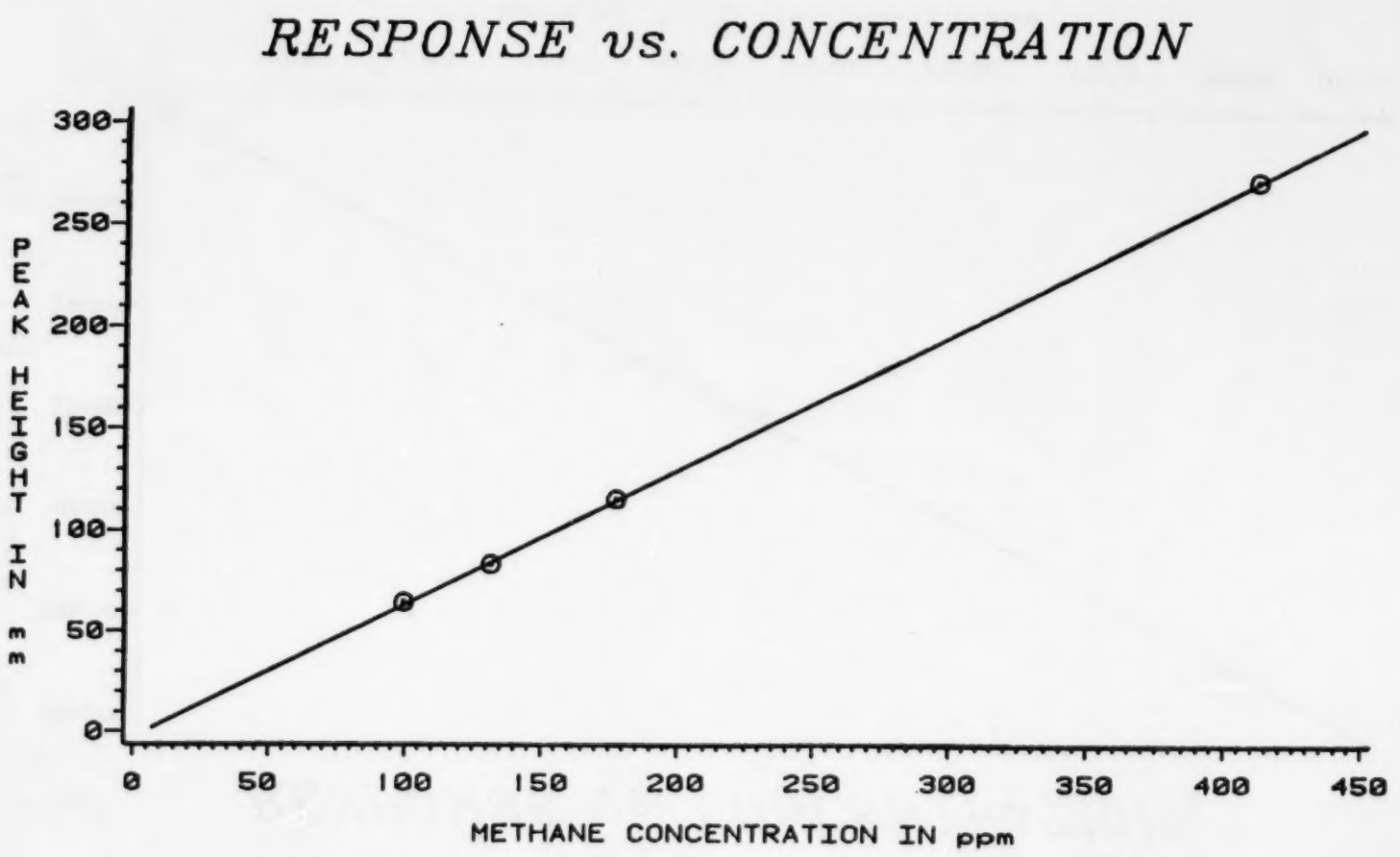


Fig. 7 Response of Methane Analytical System to Calibration Gases Ranging from 99 to 411 ppm Methane.

Table 3

Engine Specifications (Source (12))

| | |
|---|---|
| Make | Oldsmobile |
| Type | IDI, V-6 |
| Displacement | 4.3 ℓ |
| Bore | 103.05 mm |
| Stroke | 85.98 mm |
| Compression Ratio | 21.6:1 |
| Peak Torque | 226 N-m @ 1600 RPM |
| Rated Power | 63 kW @ 3600 RPM |

Brake Power (kW) at Steady State Operating Conditions

| Speed (RPM) | Fraction of Full Load | | | |
|---|---|---|---|---|
| | 0.25 | 0.50 | 0.75 | 1.00 |
| 1600 | 9.31 | 18.61 | 27.92 | 37.22 |
| 1950 | 11.05 | 22.10 | 33.15 | 44.21 |
| 2300 | 12.69 | 25.38 | 38.08 | 50.77 |

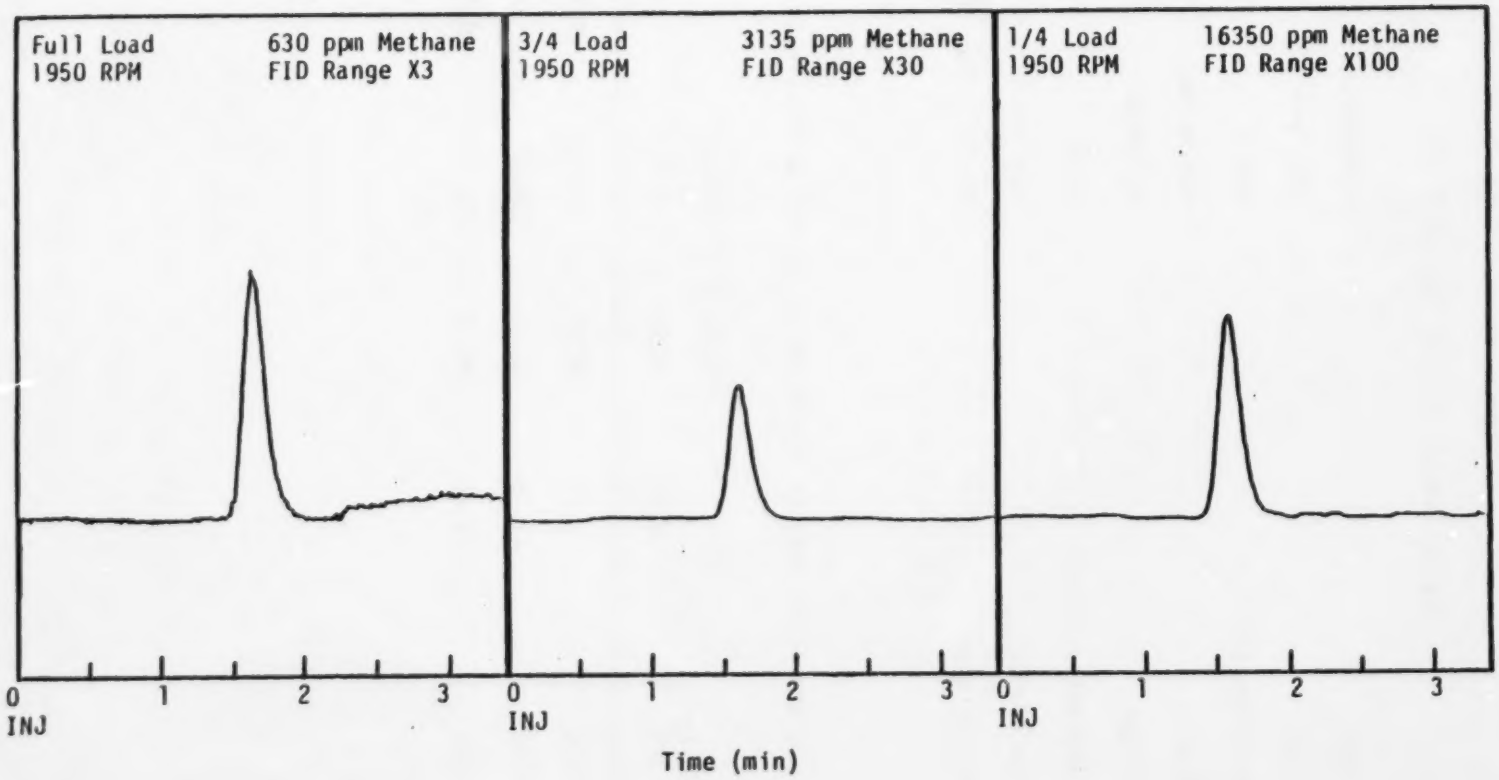


Fig. 8 Chromatograms of Diesel Engine Gaseous Exhaust Samples Using Natural Gas as a Fumigant.

The methane analytical system was calibrated during every day of Diesel engine operation. Once a preliminary calibration curve was established on a given day, the curve could be repeated for the entire duration of that day. However, the slopes of the calibration curves would be different from day to day. Over a period of three months, the slope of the curve gradually decreased from a value of 0.71 to 0.46 mm/ppm methane. However, the methane peak retention time remained precisely the same over this same time period. This gradual decrease in the FID response was most likely attributable to column deactivation. Reconditioning of the column at an elevated temperature should return the column to near its original condition. The Society of Automotive Engineers (SAE) recommends that the column be conditioned 12 hours at 150°C with carrier gas flow prior to use and at bimonthly intervals (10).

However, this recommended reconditioning was for a different type of molecular sieve column than that used in this application. The manufacturer (Supelco) of this column recommended that the column be reconditioned at 350°C for approximately 12 hours. This procedure was used in attempting to recondition the column. However, results indicated no measurable regain in the calibration curve slope. But the general shape of the methane peak was improved dramatically. The peak was noted to be much sharper with less peak width. Several attempts of continued heating at the elevated temperature failed to ever return the peak heights to their original values.

The column was opened at both ends and several inches of packing removed from each end to check for possible column contamination. Visual comparison indicated that the entrance packing was significantly darker in

color (grey-black) than the exit packing (light tan). Apparently soot in the engine exhaust was being deposited onto the column packing. The gas-phase instrumentation cart (See Ref. (11)) has a filter incorporated into the exhaust sampling line. This filter traps particles of diameters greater than 0.2 μM. If indeed soot was being deposited on the column, it must have been of submicron size (less than 0.2 μM).

Another possible explanation is that the nonmethane hydrocarbons were being condensed onto the column and backflushing failed to expulse them. Permanent absorption of nonmethane hydrocarbons appears plausible because only small detector responses were observed during column backflushing while fumigating the engine with natural gas. Large detector responses were anticipated since considerable levels of nonmethane hydrocarbons were recorded as illustrated in Fig. 9.

Although the column may have been deactivating over this time period, daily calibration of the methane analytical system accounted for the deactivation. Thus in no way does this deactivation call into question the accuracy of the engine data. In fact, excellent repeatability for virtually all engine conditions was attained in the Diesel engine study.

Figure 9 shows both methane and total unburned hydrocarbon emissions as a function of engine load. Total hydrocarbon emissions were somewhat higher than baseline DF-2 operation during fumigation at full load conditions. However, the fuel-lean mixtures at lighter loads caused excessive hydrocarbon emissions consisting mainly of unburned methane. During light load operation, the combustion temperatures are low and the ignition delay of the gaseous fumigant is longer than that of the baseline fuel (Diesel). Hence the overall combustion process appears to be

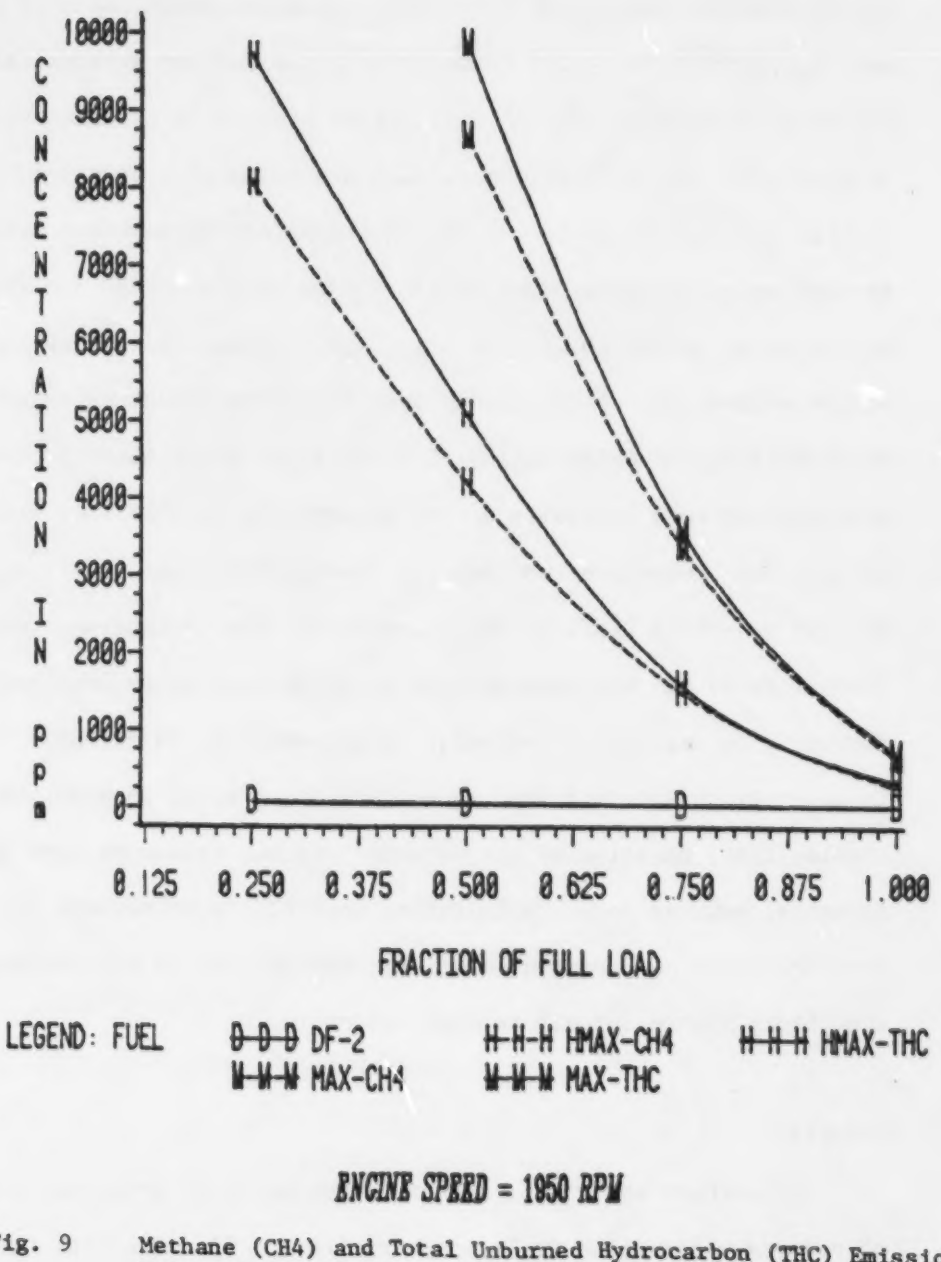


Fig. 9 Methane (CH4) and Total Unburned Hydrocarbon (THC) Emissions Versus Engine Load at the Baseline Diesel (DF-2), the Maximum (MAX) and Half-Maximum (HMAX) Gaseous Fumigation Conditions.

interrupted as reactions were effectively quenched, a result of either too low of temperature to drive the reactions, or insufficient reaction time for completion. In addition methane, the major constituent of natural gas, has a relatively slow flame speed which further accentuates the factor of time (12). As the combustible mixture is expanded and cooled, coupled with locally lean zones, bulk quenching is encountered and results in high hydrocarbon emissions consisting mainly of unburned methane. Methane emissions were found to range from as low as 250 ppm (by volume) to a high of nearly 20,000 ppm (2%), again demonstrating the applicability of the methane analytical system over a diverse operating scale. However, no methane was detected during DF-2 operation where total unburn hydrocarbons were typically around 50 ppm. It is uncertain whether no methane was present or whether its concentration was simply below the minimum detection limit of the instrument. The instruments' manual lists, "Range: Parts per million, as well as percentage concentrations - depending on analysis. Typical - 10 ppm methane, 3% methane" (13). Intuitively it was felt that no methane was present because the very stable (flat) baseline of the detector did not appear to mask any potential methane peak. With future possibility of methane being excluded from the total hydrocarbon emissions, the utility of the methane analytical system quickly becomes apparent.

## SUMMARY

The methane analytical system proved to be of great utility as part of ongoing alternative fuels investigations. Specifically, the natural

gas fumigation study revealed that exhaust hydrocarbons consisted predominately of methane. If legislation indeed comes to pass allowing methane to be excluded from total unburned exhaust hydrocarbons, an analytical means by which nonmethane hydrocarbons could be measured would become essential and invaluable. In fact, the methane analytical system appears to adequately fulfill the requirements of the above hypothetical legislation enacting automotive nonmethane hydrocarbon emissions.

The performance of the instrument itself was trouble-free. However, the loading of nonmethane hydrocarbons, soot, or other contaminants onto the column poses a problem since column reactivation was not achieved. It is not conclusive whether this phenomena was responsible for failure of column reactivation (reconditioning), but certainly warrants further investigation. If soot deposition is indeed occurring, a filtration device for submicron-sized soot (less than 0.2 μM) placed ahead of the sample inlet to the methane analytical system should minimize the onset of column contamination.

The calibration of the instrument's response was extremely linear over wide range of calibrated span gases. This response linearity certainly was enhanced by the use of sample loops as opposed to syringes as a reliable means of sample introduction. This was reflected in the sample variance where differences less than 2% standard deviations of the mean over 5 repetitive samples were encountered (see Table 2). The instrument's turn-around analysis time of five minutes was perhaps slightly too long. However, further optimization of operating parameters such as carrier flow rate and oven temperature and possibly decreasing the tube-length of the carrier flow line, would most likely decrease the turn-around analysis time. Once steady-state operation was attained on a

given day, the instrument's calibration response curve could be repeated within experimental error for the entire duration of that day, lending confidence to the Diesel engine data obtained with it. The methane analytical system proved to be most satisfactory in meeting the specific interests of this research.

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